Higher-order Diagrammatic Vibrational Coupled-Cluster Theory

Jacob Faucheaux

University of Illinois at Urbana-Champaign

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Vibrational structure theory in the harmonic approximation

- $\hat{H} = -\frac{1}{2}\sum_{i}^{N}\frac{\partial^2}{\partial Q_i^2} + V(Q)$
- $V(Q) = V_0 + \sum_{i,j} F_{ij} Q_i Q_j$
- $|\Phi_{\mathbf{s}}\rangle = \prod_i |\phi_{s_i}\rangle$

Anharmonic methods inspired by electronic structure

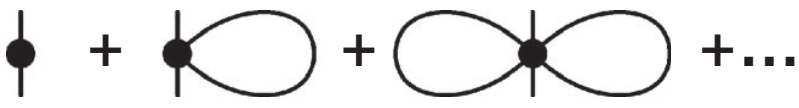
Self-Consistent Field	→	VSCF
Perturbation Theory	→	VMP2
Coupled-Cluster	→	VCC

However, above vibrational methods include non size-consistent terms, which vanish in the thermodynamic limit.

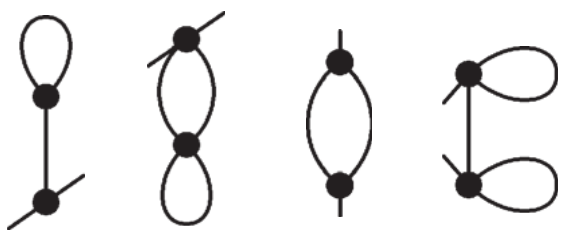
Diagrammatic Vibrational Structure Methods

Size-extensive analogs to traditional vibrational methods developed in the Hirata lab which yield efficient implementations free of numerical basis-sets.

XVSCF:[1]

$$\frac{U^{(2)}_{m,\mathbf{s}}}{2\omega_m} =$$  $$+\ \ldots$$

XVMP2:[2]



[1] Hermes, Keçeli, and Hirata *J. Chem. Phys.* **136** 234109 (2012)

[2] Hermes and Hirata *J. Chem. Phys.* **139** 034111 (2013)

Formalism of XVCC*m*

The ground state coupled-cluster wave function:

$$|\Psi_0\rangle = e^{\hat{T}}|\Phi_0\rangle$$

where $\hat{T}$ is the excitation operator that is truncated at m.

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_m$$

$$\hat{T}_n = \frac{1}{n!} \sum_{i_1,i_2,\ldots,i_n} \tau_{i_1 i_2 \cdots i_n} \{\hat{a}^\dagger_{i_1} \hat{a}^\dagger_{i_2} \cdots \hat{a}^\dagger_{i_n}\},$$

Coupled-Cluster Equations

The $\hat{T}_n$ amplitude equation of XVCCm:

$$\langle \Phi_{\nu_1 \nu_2 \cdots \nu_n} | \left(\hat{H}_N e^{\hat{T}} \right)_C | \Phi_0 \rangle = 0$$

Non-linear set of equations to be solved for τ amplitudes.

The XVCCm energy equation:[1]

$$\langle \Phi_0 | \left(\hat{H}_N e^{\hat{T}} \right)_C | \Phi_0 \rangle = \Delta E_0^{(m)}$$

[1] Shavitt and Bartlett. Many-Body Methods in Chemistry and Physics.

Equation-of-Motion XVCC for vibrational frequencies

Interested in vibrational frequency of kth excited state:

$$\omega_k^{(m)} = E_k - E_0$$

Wave function of excited state obtained by action of linear excitation operator on XVCC ground state wave function:

$$\Psi_k = \hat{R}|\Psi_0\rangle$$

$$\hat{R} = r_0 + R_1 + R_2 + \cdots + R_m$$

$$\hat{R}_n = \frac{1}{n!} \sum_{i_1, i_2, \cdots, i_n} r_{i_1 i_2 \cdots i_n} \{\hat{a}_{i_1}^\dagger \hat{a}_{i_2}^\dagger \cdots \hat{a}_{i_n}^\dagger\}$$

EOM-XVCCm equations

The $\hat{R}_n$ amplitude equation of EOM-XVCCm:

$$\langle \Phi_{\nu_1 \nu_2 \cdots \nu_n} | \left(\hat{H}_{\mathrm{N}} e^{\hat{T}} \hat{R} \right)_{\mathrm{C}} | \Phi_0 \rangle \quad = \quad \omega_k^{(m)} r_{\nu_1 \nu_2 \cdots \nu_n}$$

Solving eigenvalue problem yields desired vibrational frequencies.

Second-Quantized Normal-Ordered Vibrational Hamiltonian in a QFF[1]

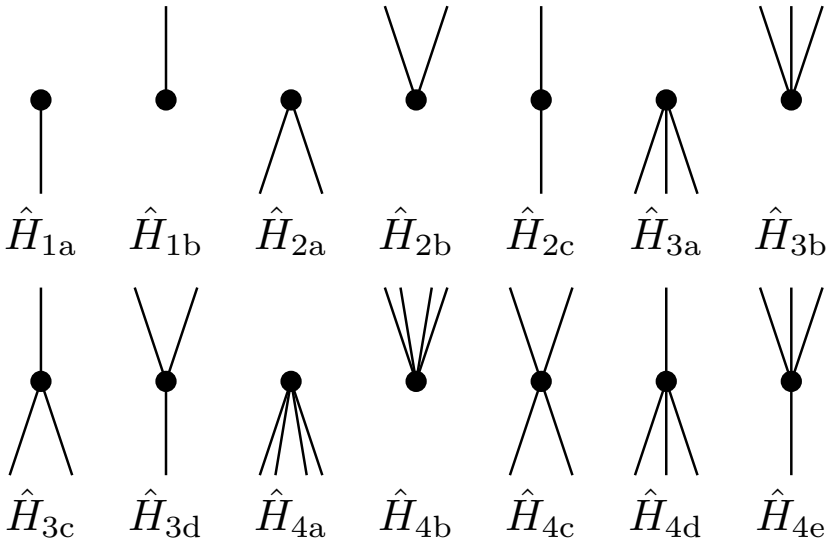
$$
\begin{aligned}
\hat{H}_N = & \sum_i W_i\{\hat{a}_i\} + \sum_i W_i\{\hat{a}_i^\dagger\} + \frac{1}{2!}\sum_{i,j} W_{ij}^-\{\hat{a}_i\hat{a}_j\} + \frac{1}{2!}\sum_{i,j} W_{ij}^-\{\hat{a}_i^\dagger\hat{a}_j^\dagger\} \\
& + \sum_{i,j} W_{ij}^+\{\hat{a}_i^\dagger\hat{a}_j\} + \frac{1}{3!}\sum_{i,j,k} W_{ijk}\{\hat{a}_i\hat{a}_j\hat{a}_k\} + \frac{1}{3!}\sum_{i,j,k} W_{ijk}\{\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k^\dagger\} \\
& + \frac{1}{2!}\sum_{i,j,k} W_{ijk}\{\hat{a}_i^\dagger\hat{a}_j\hat{a}_k\} + \frac{1}{2!}\sum_{i,j,k} W_{ijk}\{\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k\} + \frac{1}{4!}\sum_{i,j,k,l} W_{ijkl}\{\hat{a}_i\hat{a}_j\hat{a}_k\hat{a}_l\} \\
& + \frac{1}{4!}\sum_{i,j,k,l} W_{ijkl}\{\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k^\dagger\hat{a}_l^\dagger\} + \frac{1}{2!}\frac{1}{2!}\sum_{i,j,k,l} W_{ijkl}\{\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k\hat{a}_l\} \\
& + \frac{1}{3!}\sum_{i,j,k,l} W_{ijkl}\{\hat{a}_i^\dagger\hat{a}_j\hat{a}_k\hat{a}_l\} + \frac{1}{3!}\sum_{i,j,k,l} W_{ijkl}\{\hat{a}_i^\dagger\hat{a}_j^\dagger\hat{a}_k^\dagger\hat{a}_l\}
\end{aligned}
$$

[1] Hirata and Hermes. *J. Chem. Phys.* **141** 184111 (2014)

W amplitudes are sums of scaled force constants

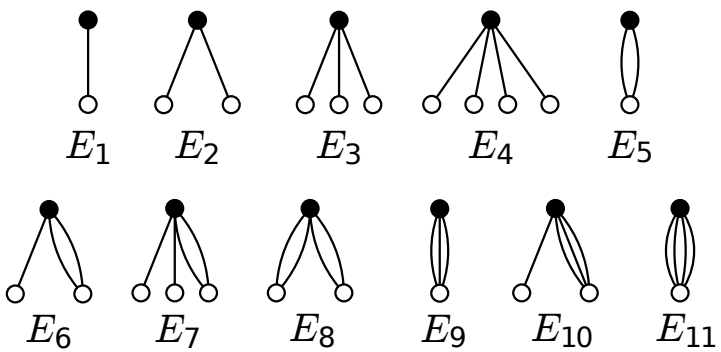
$$
\begin{aligned}
W_i &= \frac{F_i}{(2\omega_i)^{1/2}} + \frac{1}{2}\sum_j \frac{F_{ijj}}{(2\omega_i)^{1/2}(2\omega_j)} + \cdots, \\
W_{ij}^{\pm} &= \pm\frac{1}{2}\delta_{ij}\omega_i + \frac{F_{ij}}{(2\omega_i)^{1/2}(2\omega_j)^{1/2}} \\
&\quad + \frac{1}{2}\sum_k \frac{F_{ijkk}}{(2\omega_i)^{1/2}(2\omega_j)^{1/2}(2\omega_k)} + \cdots, \\
W_{ijk} &= \frac{F_{ijk}}{(2\omega_i)^{1/2}(2\omega_j)^{1/2}(2\omega_k)^{1/2}} + \cdots, \\
W_{ijkl} &= \frac{F_{ijkl}}{(2\omega_i)^{1/2}(2\omega_j)^{1/2}(2\omega_k)^{1/2}(2\omega_l)^{1/2}} + \cdots.
\end{aligned}
$$

Diagrammatic Representations



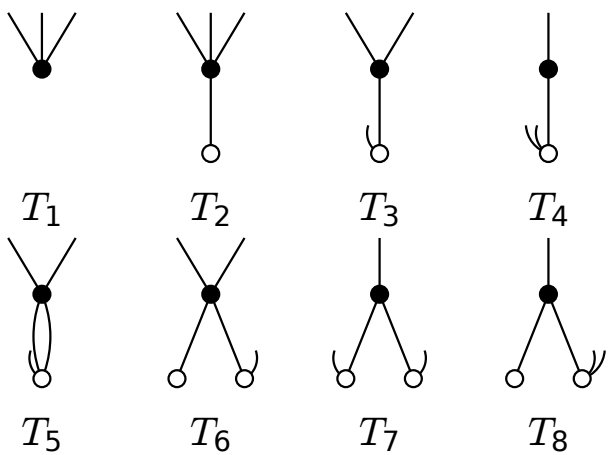
Energy diagrams of XVCCm in nth-order PES

1. Draw an $\hat{H}_{\mathrm{N}}$ vertex having up to n lines.
2. Draw 1 to n $\hat{T}_k$ vertices $(1 \leq k \leq m)$ beneath the $\hat{H}_{\mathrm{N}}$ vertex.
3. Connect the lines of the $\hat{T}_k$ vertices with the lines of the $\hat{H}_{\mathrm{N}}$ vertex without altering line directions, leaving zero external lines to form a connected diagram.
4. Repeat steps 1–3 to enumerate all topologically distinct diagrams.



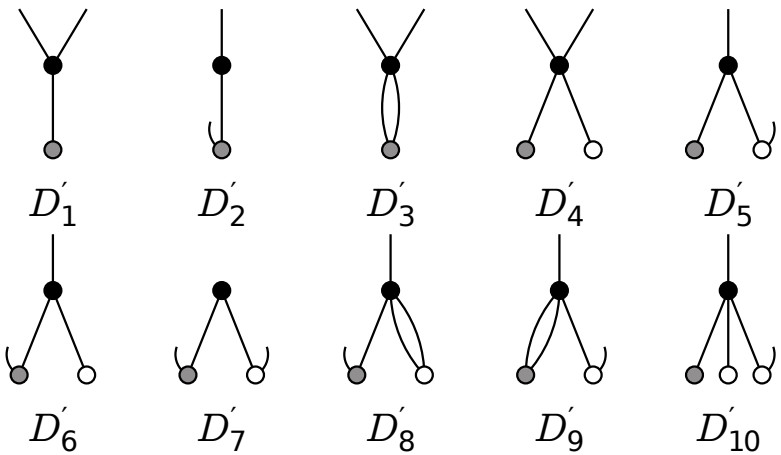
$\hat{T}_l$ amplitude diagrams of XVCCm in nth-order PES

1. Draw an $\hat{H}_\mathrm{N}$ vertex having up to n lines.
2. Draw 0 to n $\hat{T}_k$ vertices ($1 \leq k \leq m$) beneath the $\hat{H}_\mathrm{N}$ vertex.
3. Connect the lines of the $\hat{T}_k$ vertices with the lines of the $\hat{H}_\mathrm{N}$ vertex without altering line directions, leaving l external lines to form a connected diagram.
4. Repeat steps 1–3 to enumerate all topologically distinct diagrams.



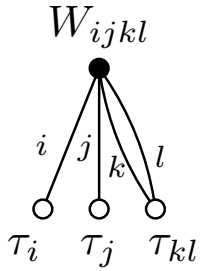
$\hat{R}_l$ amplitude diagrams of EOM-XVCCm in nth-order PES

1. Draw an $\hat{H}_{\mathrm{N}}$ vertex having up to n lines.
2. Draw an $\hat{R}_h$ vertex $(1 \leq h \leq m)$ and zero to $(n-1)$ $\hat{T}_k$ vertices $(1 \leq k \leq m)$ beneath the $\hat{H}_{\mathrm{N}}$ vertex.
3. Connect the lines of the $\hat{R}_h$ and $\hat{T}_k$ vertices with the lines of the $\hat{H}_{\mathrm{N}}$ vertex without altering line directions, leaving l external lines to form a connected diagram.
4. Repeat steps 1–3 to enumerate all topologically distinct diagrams.



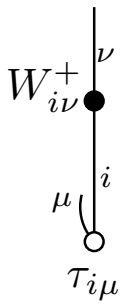
Algebraic interpretation of XVCC diagrams

XVCC Energy Diagrams:



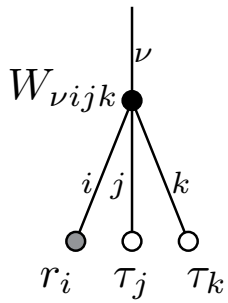
$$\frac{1}{2!}\frac{1}{2!}\sum_{i,j,k,l} W_{ijkl}\tau_i\tau_j\tau_{kl}$$

XVCC Amplitude Diagrams:



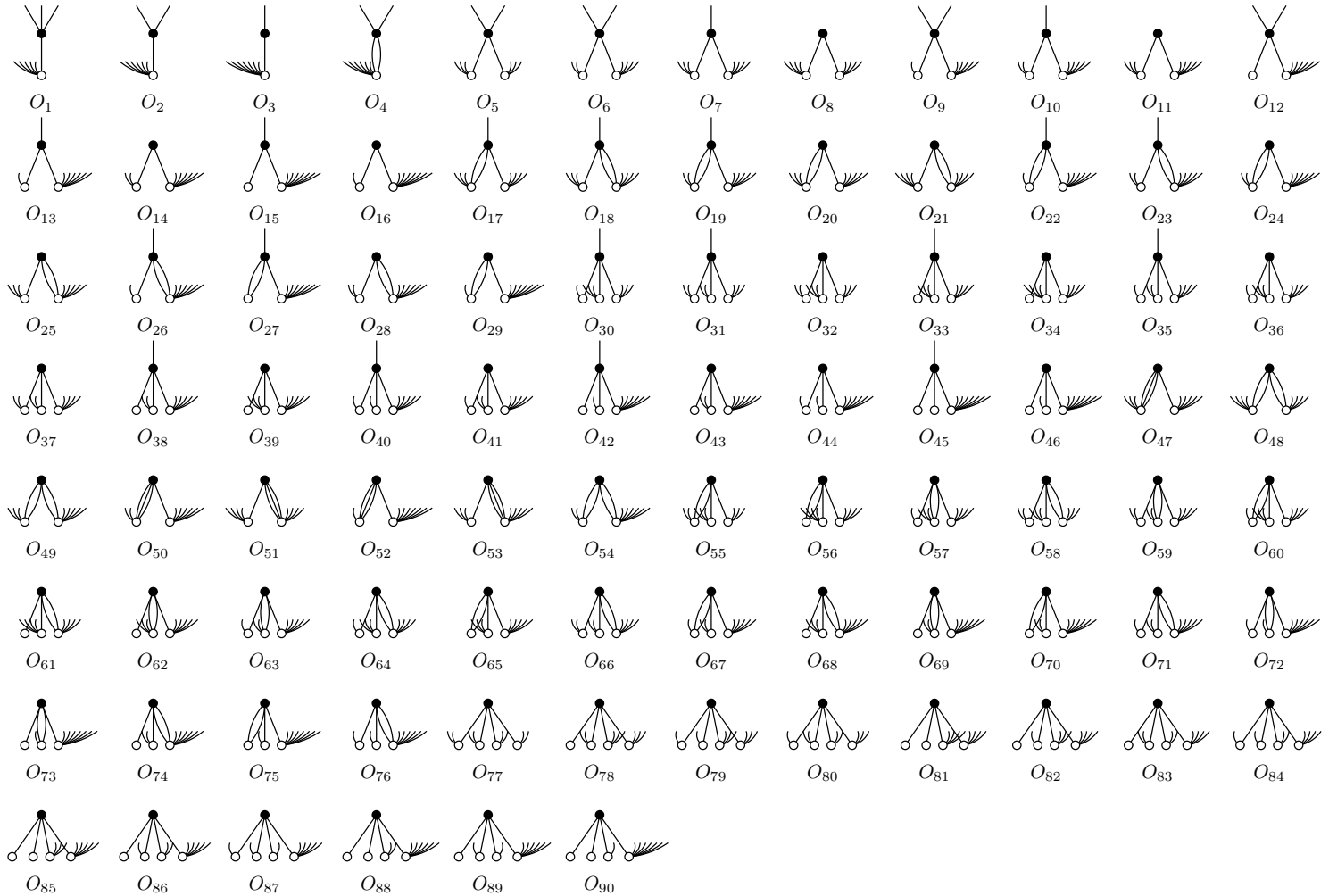
$$\hat{P}(\nu\mu)\sum_i W^+_{i\nu}\tau_{i\mu} = \sum_i W^+_{i\nu}\tau_{i\mu} + \sum_i W^+_{i\mu}\tau_{i\nu}$$

EOM-XVCC Amplitude Diagrams:



$$\frac{1}{2!}\sum_{i,j,k} W_{\nu ijk}r_i\tau_j\tau_k$$

Automatic Derivation of XVCC equations



Automatic Algorithm Optimizations

- Algorithm optimizations known as strength reduction, intermediate reuse, and factorization performed.[1]
- For a quartic force field, scaling of XVCCm and EOM-XVCCm reduced from $O(N^{m+4})$ to $O(N^{m+2})$
- EOM-XVCC8 calculations on the water molecule sped up from about 12 hours to a few seconds.

[1] Hirata J. Phys. Chem. A **107** 9887-9897 (2003)

Numerical results for the water molecule

The calculated zero-point energy (E_0) and frequencies (ν_i) of the fundamental transitions (in cm^{-1}) of the water molecule. Except for VCI, the errors from VCI are shown.

Method	E_0	ν_1	ν_2	ν_3
VCI	4642.4	3682.4	1556.6	3791.5
XVSCF[4]	21.5	105.3	11.7	116.1
XVCCS[4]	21.5	105.3	11.7	116.1
XVCCSD[4]	21.5	26.0	6.8	26.6
XVCCSDT[4]	0.4	–1.7	2.4	–1.9
XVCCSDTQ[4]	0.0	–0.1	0.1	–0.1
XVMP2[4]	–1.3	–14.8	2.5	–17.0

Accurate overtone and combination transitions with EOM-XVCC*m*

The calculated frequencies of selected overtones and combinations (in cm^{-1}) of the formaldehyde molecule. Except for VCI, the errors from VCI are shown.

Method	(000200)	(000101)	(001100)	(002000)	(000300)	(000201)
VCI	2318.1	2399.6	2660.6	3000.8	3464.2	3555.2
EOM-XVCCSD[4]	35.7	28.3	77.7	23.2	...	...
EOM-XVCCSDT[4]	7.6	6.0	5.7	4.7	62.5	49.6
EOM-XVCCSDTQ[4]	2.1	2.0	2.0	2.0	14.2	10.9
EOM-XVCC5[4]	0.1	0.1	0.1	0.2	3.3	3.0
EOM-XVCC6[4]	0.0	0.0	0.0	0.0	0.5	0.3
EOM-XVCC7[4]	0.0	0.0	0.0	0.0	0.1	0.1
EOM-XVCC8[4]	0.0	0.0	0.0	0.0	0.0	0.0

Acknowledgements

- So Hirata
- Matt Hermes
- Hirata Group
- NSF GRFP

Formaldehyde Molecule

The calculated zero-point energy (E_0) and frequencies (ν_i) of the fundamental transitions (in cm^{-1}) of the formaldehyde molecule. Except for VCI, the errors from VCI are shown.

Method	E_0	ν_1	ν_2	ν_3	ν_4	ν_5	$\nu_3\nu_6$	$\nu_2\nu_6$	ν_6
VCI	5813.6	2837.2	1719.8	1501.5	1160.7	2873.3	2702.8	2989.2	1237.5
XVSCF[4]	22.9	79.0	20.4	9.8	10.6	106.7	...	...	11.2
XVCCS[4]	22.9	79.1	20.9	9.3	10.6	106.7	...	...	11.1
XVCCSD[4]	22.9	24.2	6.0	4.2	6.0	31.0	35.5	33.0	5.6
XVCCSDT[4]	0.8	0.1	0.5	1.2	1.9	1.3	6.1	1.4	1.4
XVCCSDTQ[4]	0.1	0.2	0.0	0.1	0.0	0.7	2.3	1.0	0.0
XVMP2[4]	–1.0	–8.9	0.3	1.4	1.5	2.2	18.0	24.8	1.8